Growth and Characterization of SnO_2 micro- and nanotubes

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Abstract. Micro- and nanotubes, and other elongated structures of SnO_2 as wires and rods, were grown after sintering in argon flow at temperatures ranging from 1350ºC to 1500ºC. The morphology and luminescence properties of these structures have been investigated by means of the secondary electron and the cathodoluminescence (CL) modes of the scanning electron microscope (SEM).

INTRODUCTION

Fabrication and characterization of semiconductor structures in form of nanowires, nanorods and nanotubes is a subject of increasing interest due to the potential application of the nanostructures in future nanoelectronic systems. In the case of semiconductors with gas sensing applications, as SnO_2, the high surface to volume ratio of the nanostructures provides a high sensitivity to the interaction with gases. SnO_2 is also a promising material for optoelectronic devices. Recently SnO_2 nanowires and belts, and discontinous tubular structures have been grown by thermal evaporation of powder on a substrate [1].

In this work the growth of micro and nanotubes and other elongated structures of SnO_2 during sintering treatments is investigated. The samples were characterized by means of the secondary electron and cathodoluminescence (CL) modes in the scanning electron microscope (SEM).

EXPERIMENTAL

The starting material used was commercial SnO_2 powder, formed by particles and aggregates of rounded particles with sizes of about 200 nm. Samples were prepared by compacting the powder under a compressive load of 2 tons to form disks. The powder was either untreated or mechanical ball milled, which leads to smaller and more homogeneous particle size. The samples were sintered in argon flow at temperatures from 1000 ºC to 1500 ºC. CL measurements were performed with a LEICA 440 SEM at a temperature of 80 K and accelerating voltages ranging from 12 KV to 18 KV. Spectra were recorded with a charge coupled device (CCD) camera with a built in spectrograph (Hamamatsu PMA-11).

RESULTS

Sintering under argon flow at temperatures between 1350 ºC and 1500 ºC leads to the formation of wires, rods and tubes with lateral dimensions ranging from tens or hundreds of nanometers to some micrometers, as shown in Fig. 1.

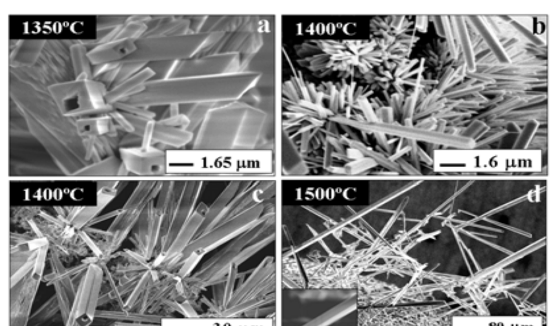

FIGURE 1. Micro and nanostructures grown after treatments in argon flow at different temperatures.

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Sintering at 1500 ºC causes the formation of a wire-like structure on the sample surface. Typical cross-sectional dimension of the wires is several microns and the length is of hundreds of microns or even reach the millimeter range. The wires show a higher luminescence than the sample background (Fig. 2). The CL spectra reveal the presence of a band at 1.94 eV in the wires, related to the oxygen vacancies [2].

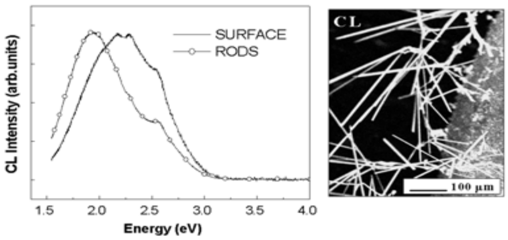

FIGURE 2. CL spectra and image of the surface of a sample sintered at 1500ºC in Ar flow

In the samples prepared at temperatures between 1350 ºC and 1450 ºC micro and nanorods with rectangular cross-section are observed. Some of the rods have a tubular structure with a hollow and well defined lateral faces (Fig. 1a, 1c and Fig. 3). In samples prepared from ball milled powder, a more regular distribution of the structures is obtained.

The external faces of the tubes are normally flat, while the interior can present different appearances (scaled as seen in Fig. 3a, or oriented layered as Fig. 3b shows), depending on the stage of the growth process.

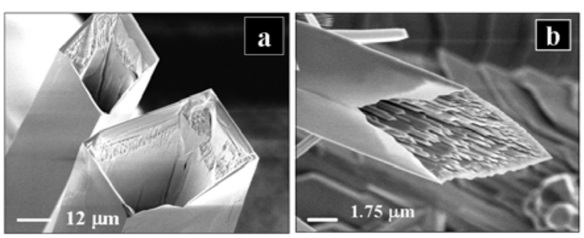

FIGURE 3. SEM images of tubes showing inner scaled (a) and oriented layered nanostructure (b).

According to ref. [3], the most probable growth direction seems to be the [101]. Lateral surfaces of the rectangular tubes would be the (010) and the (10-1). The presence of tubes with high dimensions enables to record spectra in different crystal faces as well as in the tube interior. The inner surfaces of the tubes show a more intense CL emission with a peak at 2.58 eV, while the spectra of the external surfaces reveal in addition the presence of the 1.94 eV band (Fig. 4).

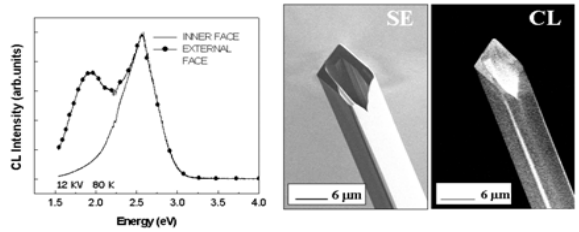

FIGURE 4. CL spectra recorded in different tube faces (internal and external) and SE and CL images.

Some samples sintered at 1350 ºC show a surface structure (Fig. 5) which is thought to be the first steps of the growth of the elongated structures.

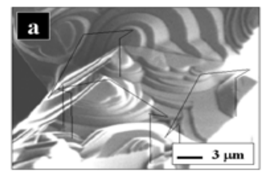

FIGURE 5. First steps of the growth process

CONCLUSIONS

Sintering SnO_2 compacted disks under argon flow in the temperature range from 1350ºC to 1500ºC leads to the formation of wires, rods and tubes on the sample surface. Since not a catalytic process or a foreign substrate is involved, it appears that the formation of the structures takes place by a vapor-solid process. Enhanced luminescence emission arises from the internal region of the tubes, which is of potential application in high resolution displays.

ACKNOWLEDGMENTS

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REFERENCES

1. Pan,Z.W, Dai, Z.R Wang,Z.L, *Science* **291** 1947-1949 (2001)
2. Maestre, D., Cremades, A. and Piqueras, J. *J.Appl.Phys*. **95**, 3027-3030 (2004)
3. Beltrán, A. Andrés, J., Longo, E. and Leite, E.R. *Appl Phys. Lett.* **83**, 635-637 (2003)